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PEDOT:PSS/Grafted-PDMS Electrodes for Fully Organic and Intrinsically Stretchable Skin-like Electronics

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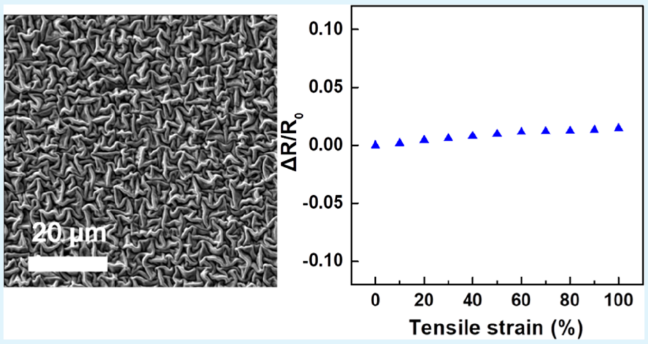
Supporting Information

ABSTRACT: Skin-like electronics require materials that are conducting, soft, intrinsically stretchable, and highly robust. However, electronic devices often consist of multilayers, and the failure of the electronic devices mostly starts from the debonding of the layers because of poor interfacial adhesion and large mechanical mismatch. Herein, we introduce a fully organic and intrinsically stretchable electrode that achieves high robustness by grafting the substrate to improve the interfacial adhesion and by introducing deep folds and wrinkles to improve the stretchability. The electrode exhibits a sheet resistance of 90 Ω/□ and negligible change in resistance at strains of up to 100% and shows no fatigue over 10 000 cyclic stretches to 100% strain. An iontronic skin with the electrodes is capable of detecting tiny objects exemplified by walking ants or fruit flies weighing less than 1 mg, and the device can be cyclically stretched to 30% for 1000 times without fatigue. The high robustness and stretchability of the fully organic iontronic skin lie in the wrinkle structures, small mechanical mismatch, and high interfacial strength among different layers. This work offers a general way to fabricate highly stretchable and robust devices.



KEYWORDS: *interfacial adhesion, stretchability, fully organic system, sensitivity, skin-like electronics*

INTRODUCTION

The recent years have witnessed the fast development of flexible electronics. Especially, skin-like electronics that are highly conformable and highly stretchable are desired in epidermal health monitoring, human−machine interface, and wearable devices.[1−7] However, few materials are mechanically stretchable and electrically functional simultaneously. The leap from the conventional electronics of brittle materials to the next-generation flexible electronics requires a lot of efforts to reform the device and the design of material, for example, to make sensors with large stretchability and high robustness like our skin.

A flexible electrode is a key component for flexible devices[8−10] and can typically be fabricated by depositing or transferring a conducting film onto the surface of an elastomeric substrate. There are many conductors such as carbon nanotubes, graphene sheets, gold nanomeshes, silver nanowires, and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, the most widely used conductive polymer) that have been used as flexible electrodes.[11−16] For stretchable substrates, polydimethylsiloxane (PDMS) is one of the most common selections because of its high transparency, high elastic limit, and excellent stability.[8] Because of the large difference in mechanical properties as well as the different surface properties between the metal/carbon conductors and the elastomeric substrate, debonding or delamination often happens when the electrodes are subjected to cyclic stretching or other harsh conditions. Once debonding or delamination happens, the conductive film breaks at a quite small strain. This flaw limits the real applications of flexible electrodes and devices.[17] Fully organic electrodes present advantages of simple fabrication, low cost, and large flexibility over metal electrodes. However, they still suffer from poor interfacial adhesion and thus limited stretchability. For instance, few PEDOT:PSS/PDMS electrodes can maintain conducting at 100% tensile strain, or subjected to cyclic stretches to large strains.[18,19] This problem becomes more serious because PDMS is a hydrophobic material while conducting polymers are typically hydrophilic, and the difference results in insufficient interfacial strength between PDMS and the

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conductor, which will reduce the long-term stability of the electrode. In this sense, we need to explore a technique to improve the stretchability and interfacial adhesion of organic conductive films, which can be further used in stretchable electronic devices and systems.

Herein, our strategy is to introduce hydrogen bonds to improve interface strength, as well as to generate deep folds and wrinkles to enhance the stretchability of the electrode. We fabricated a high-performance PEDOT:PSS/PDMS electrode by transferring the PEDOT:PSS conducting film to a biaxially prestrained substrate, and the electrode was successfully used for skin-like electronics. In this work, we improve the stretchability and stability of the electrode by grafting poly(methacrylic acid) (PMAAc) on the PDMS surface, which forms strong interaction with the PEDOT:PSS film by forming hydrogen bonds and by introducing deep folds and wrinkles of the conducting layer. The obtained electrode shows high conductivity with a sheet resistance of 90 $\Omega/\square$, high stretchability of up to 100% strain without loss of conductivity, and high robustness that is free of fatigue after 10 000 cycles of stretching to 100%. We also show that the electrode is potentially useful in fully organic and intrinsically stretchable electronics: iontronic skins applying this electrode exhibit a maximum sensitivity of 7.00 kPa^{-1}, and show no performance degradation after cyclic stretching to 30% strain. The skins are capable of detecting tiny objects such as a walking ant or fruit fly with a mass smaller than 1 mg. The high robustness and stretchability of the fully organic e-skin lies in the small mechanical mismatch and high interfacial strength among different layers. Our work may offer a general design strategy for stretchable electronics.

■ RESULTS AND DISCUSSION

The fabrication of the electrode is illustrated in Figure 1a. First, we spin-coated a PEDOT:PSS film on a piece of clean glass followed by a sulfuric acid treatment to increase the conductivity of the PEDOT:PSS film. The conductive film has a thickness of ~50 nm and a conductivity of 2200 S/cm. Next, we applied photo-initiated polymerization to graft a hydrophilic polymer PMAAc on the surface of PDMS (Figure S1).[20,21] The grafted PDMS (g-PDMS) shows a water contact angle of 68° without damaging other merits of PDMS (Figure S2). Finally, the treated PEDOT:PSS was transferred to a biaxially prestrained g-PDMS substrate (Figure S3). The electrode is in light blue as shown in Figure 1b. Figure 1c shows the chemical structure of PEDOT:PSS and g-PDMS, and Figure 1d illustrates the interfacial interaction of the two electrodes with nontreated PDMS and g-PDMS as the substrate. PMAAc forms covalent bonds with the polymer backbone of PDMS to introduce abundant −COOH on the surface, which can interact with PEDOT:PSS via relatively strong hydrogen bonding. By contrast, the nongrafted PDMS surface is terminated with −CH$_3$ and forms weak interaction (van der Waals force) with PEDOT:PSS.

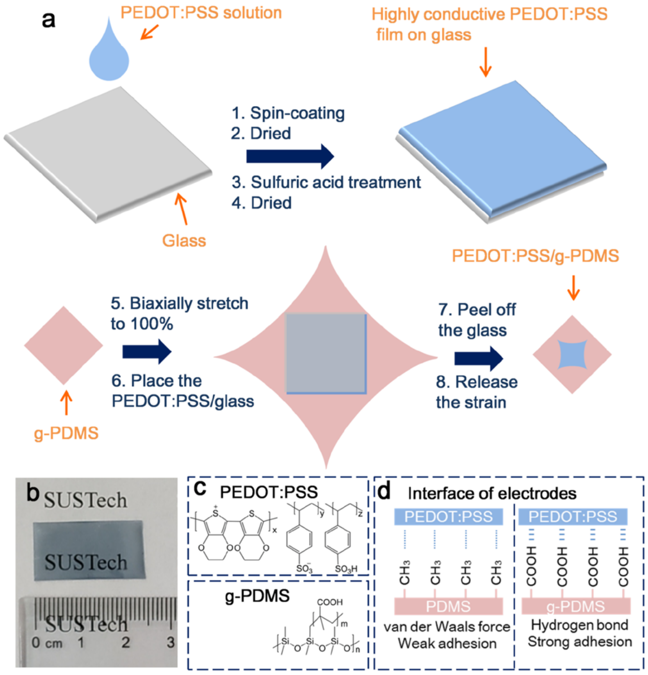

Figure 1. Schematic diagram of the fabrication of PEDOT:PSS/g-PDMS and the structure of the electrode. (a) Stepwise illustration of the preparation of the electrode. (b) Photo of the electrode. (c) Molecular structures of the conductor and the substrate. (d) Interface of the electrodes with different substrates.

The electrode shows a low sheet resistance of 90 $\Omega/\square$ and outstanding flexibility; it exhibits negligible change in resistance (normalized change in resistance is less than 2%) when bent at a bending radius of 1 mm, or when stretched to an extreme large strain of 100% (Figure 2a,b). The electrode is also highly robust under cyclic bending or stretching tests: after 10 000 times of bending at a radius of 1 mm or 10 000 stretches at a strain of 100%, the normalized change in resistance during the cyclic tests is still within 2% (Figure 2c,d).

The large stretchability is related to the surface microstructures of the conductive polymer. Although the prestrained PDMS surfaces are flat (Figure S4), the PEDOT:PSS/g-PDMS film forms dense wrinkles with an average wavelength of 3.22 μm and an average depth of 0.86 μm (see Figures 2e,f, and S5) when relaxed from a biaxially prestretched state. Surface wrinkles of a bilayer system have been proven to be effective to improve the stretchability.[22] The wrinkles get aligned as the electrode is uniaxially stretched without exhibiting any cracks even after 10 000 cycles of stretches to 100% strain (Figure 2f). Compared to other reported PEDOT:PSS/PDMS electrodes that are free of wrinkles,[18,19,23−25] our electrode exhibits lower sheet resistance, larger stretchability, and higher robustness.

The surface property of PDMS is of great importance. Coating or direct transferring a PEDOT:PSS film to PDMS is infeasible because of the hydrophobic nature of PDMS and the poor interfacial interaction (see Figure S6). Plasma activation and ultraviolet/ozone treatment are often used to improve the hydrophilicity of PDMS. However, these treatments are temporary and insufficient.[26] For instance, plasma-treated PDMS (p-PDMS) recovers hydrophobic within just 1 day (see Figure S7). Meanwhile, these hydrophilic treatments do not provide adequate interfacial adhesion to the PEDOT:PSS. For example, we show in Figure S8 that a spin-coated PEDOT:PSS film on p-PDMS can be easily peeled off by using a 3M scotch tape because of the poor adhesion. By contrast, the g-PDMS surface is hydrophilic and it allows PEDOT:PSS to form hydrogen bonds with the substrate. As a result, the PEDOT:PSS/g-PDMS electrode exhibits strong interfacial adhesion that can withstand taping (Figure S8).

The strong interfacial interaction is also critical to the stretchability of the PEDOT:PSS/g-PDMS electrode. A strong

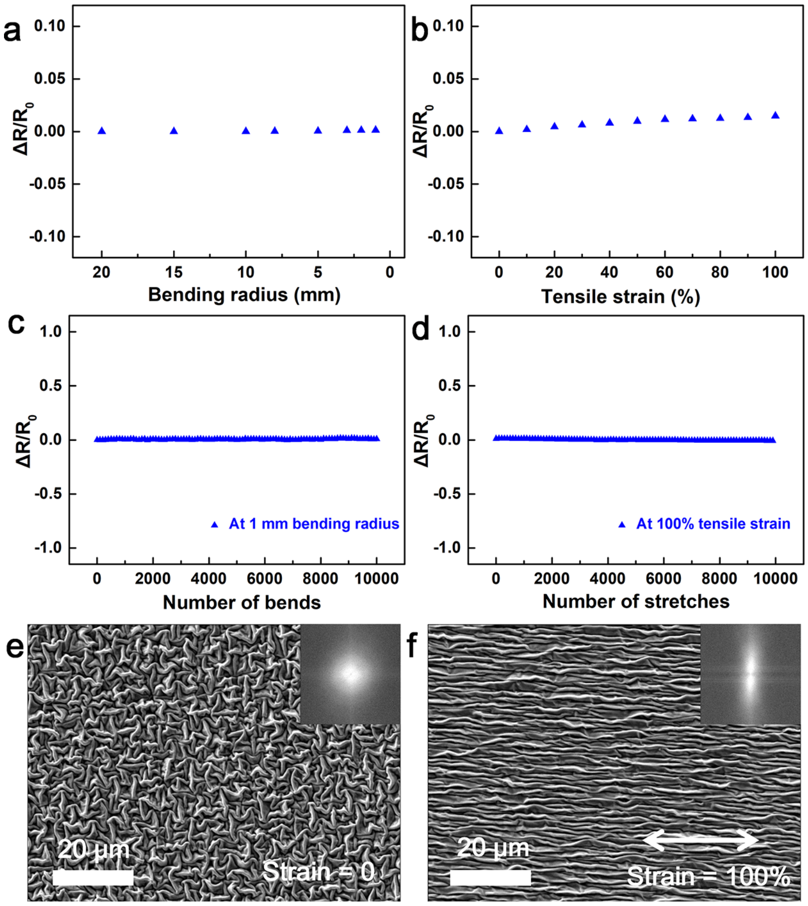

Figure 2. Performance and morphology of the PEDOT:PSS/g-PDMS electrode. (a) Resistance change of the electrode as a function of bending radii. (b) Evolution of the resistance of PEDOT:PSS/g-PDMS over the strain range from 0 to 100%. (c,d) Change of resistance of the electrode at 1 mm bending radius and at 100% tensile strain over 10 000 cycles. (e,f) Scanning electron microscopy (SEM) images of the surface of the electrode at 0 and at 100% strain. The inset pictures show the Fourier transform of the SEM images.

interface ensures that the applied stresses are uniformly distributed through the entire film to avoid the localized strain distribution and therefore delays the occurrence of cracks.[17] This effect has been evidenced in our experiment: a PEDOT:PSS film generates cracks at 12% strain on UV−ozone-treated PDMS,[27] but the crack onset strain increases to 30% on the g-PDMS. The strong interface, on the other hand, suppresses the delamination between the conductive polymer film and the substrate under large strains or cyclic deformation, and thus enhances the robustness of the electrode.[28]

We have found that the biaxially prestrained electrode performs better than the uniaxially prestrain electrode in terms of stretchability and reliability. In the case of uniaxial prestrain, the Poisson's effect will lead to lateral contraction of the substrate. PDMS is an incompressible material, thus the lateral contraction of PDMS can be expressed as: $\varepsilon_y = (1/(1+\varepsilon_x))^{0.5} - 1$, where ε_x is the prestrain of PDMS and ε_y is the strain in the lateral direction. After transferring the PEDOT:PSS film to the prestrained PDMS followed by releasing, the conducting layer codeforms with the substrate and is subjected to lateral expansion. In other word, the PEDOT:PSS film is stretched in the transverse direction. When the substrate returns to the initial state, the final lateral strain in the PEDOT:PSS film can be expressed as: $\varepsilon = \frac{1}{1+\varepsilon_y} - 1$. The conducting polymer film cracks as this strain exceeds the elastic limit of PEDOT:PSS. We did observe cracks in the released PEDOT:PSS film when the uniaxial prestrain is beyond a certain value. On the untreated PDMS, the PEDOT:PSS film cracks at a prestrain of ~20%, while that for g-PDMS increases to ~70% (Figure S9). When the electrodes with uniaxially prestrained PDMS are subjected to the cyclic tensile test beyond the prestrain, cracks form and propagate, leading to the increases of resistance. In Figure S10, we can see that the resistance of the uniaxially prestrain electrode increases 40% after 7000 cyclic stretches to the prestrain, and correspondingly optical microscopy (OM) images shows a lot of cracks along the tensile direction. In brief, it is the Poisson's effect that limits the stretchability and stability of uniaxially prestrain electrodes. The biaxially prestrained electrode well solves this problem because the conductive film will not be in tension in both directions. As a result, the electrode can survive at larger strains, as evidenced in Figure 2.

We have also applied the PEDOT:PSS/g-PDMS electrode in e-skins to ensure its potential in stretchable electronics. The skin was constructed by two PEDOT:PSS/g-PDMS electrodes sandwiching an ionic gel with a microstructured surface (Figure 3a,b). The bottom surface of the ionic gel is flat while the top surface of the ionic gel has uniformly distributed microcones. The average height of the microcones is ~25 μm and the average distance between neighboring microcones is ~34 μm. Electric double layers (EDLs) form at the electrode−gel interfaces, and the capacitance of the sensor is proportional to the contact area of EDLs of the rough side. Upon

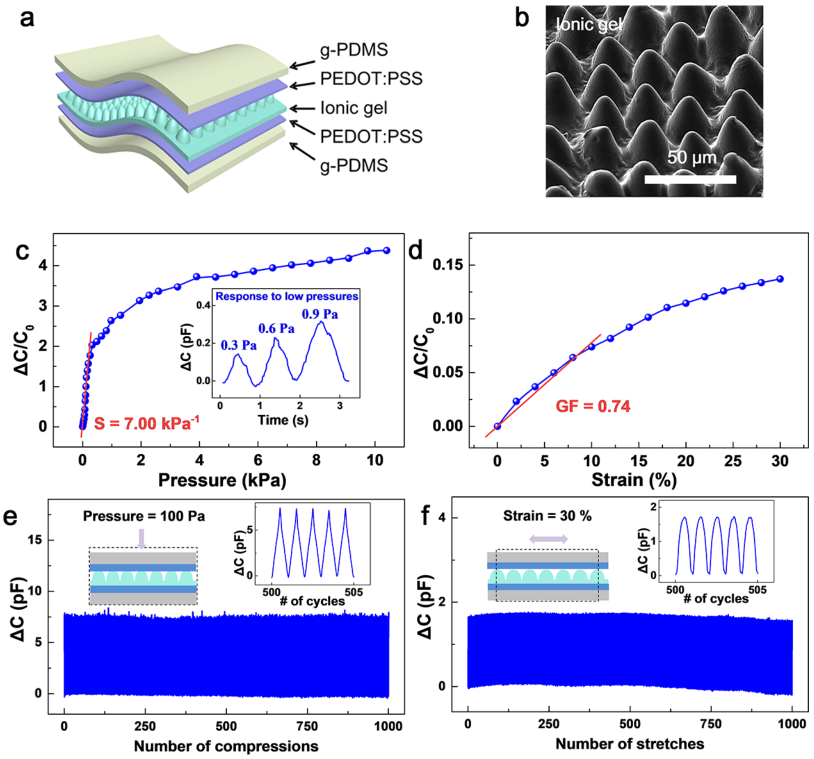

Figure 3. Sensitivity and cyclic stability of the iontronic skin. (a) Structure of the sensor. (b) Scanning electron microscopy image of the ionic gel. (c) Normalized change in capacitance as a function of pressure over 0−10 kPa of the sensor, showing a maximum sensitivity of 7.00 kPa^{-1}. The inset shows the signal at low pressures down to 0.3 Pa. (d) Normalized change in capacitance as a function of strain of the sensor by stretching to 30%. (e) Capacitance signal over 1000 compression cycles under 100 Pa. (f) Capacitance signal over 1000 stretching cycles to 30% strain. The insets in panels (e,f) show the output patterns during the compression and stretching test.

compression, the contact area between the microcones and electrode increases, leading to the increase of capacitance accordingly. Moreover, stretching or bending in a multilayer system will also cause compressive stresses in the middle layer, thus the capacitance changes upon deformation.

The sensor shows a relatively high capacitance to pressure sensitivity (which can be expressed as the normalized change in capacitance $\Delta C/C_0$ over the change in pressure ΔP, $S = \Delta C/(C_0 \Delta P)$) of 7.00 kPa^{-1} at the low-pressure region (<350 Pa). The sensitivity decreases in the higher pressure region. The sensor also exhibits a limit of detection (LOD) as low as 0.3 Pa—it shows that the sensor well responds to low-pressure input (from 0.3 to 0.9 Pa) and gives clear output signals with a high signal to noise ratio, as presented in the inset of Figure 3c. Here 0.3 Pa is the minimum pressure we can apply with our machine, and we believe that the actual LOD of the device should be even smaller. Other than normal compression, the sensor also well responds to uniaxial strains up to 30% with an average gauge factor (GF) ∼0.47 and a maximum GF of 0.74 (from 0 to 10% strain) (Figure 3d). This allows our sensor to detect both stretching and normal pressure signals simultaneously, for example, pressing the sensor when it is stretched will generate an increased signal amplitude (Figure S11). By contrast, few e-skins or pressure sensor could well detect both normal pressure and in-plane strain. Compared with other stretchable capacitive-type stretchable sensors, the GF of our sensor (0.74) is quite close to the reported results, including e-skins with carbon nanotube electrodes and elastomeric dielectric, and silver network electrode sandwiching a polyurethane matrix.[11,29−31] The stretchability of this sensor is limited by the ionic gel layer. When dielectric layer is replaced by PDMS and then the new sensor can respond to an external strain of up to 100% but with a much smaller sensitivity, as shown in Figure S12. Moreover, the device exhibits high stability under cyclic compression/releasing or stretching/releasing. The high stability under cyclic compression or stretches of the sensor is presented in Figure 3e,f, showing little change of the signal after 1000 cycles of compression (100 Pa)/releasing or after 1000 stretching cycles to 30% strain, respectively.

The large stretchability stems from the surface instabilities, while the high reliability under cyclic stretches is related to the fully organic nature. Organic materials typically have a far smaller elastic modulus than metals or carbon materials. In our sensor, PDMS and ionic gel in this study have an elastic moduli of 1−2 MPa, and although the PEDOT:PSS film presents an elastic modulus on the order of 1 GPa, its small thickness (∼50 nm) and high interfacial strength guarantees high stability of the interface. By contrast, metals often have a Young's modulus of ∼100 GPa, which is two orders of magnitude higher than that of PEDOT:PSS and five orders of magnitude higher than that of PDMS. The large mechanical mismatch between the metal and PDMS will easily lead to the failure of the metal/PDMS interface upon cyclic deformations.[17] In a bilayer system with surface wrinkles, debonding or delamination is caused by the interfacial shear stresses, which are directly correlated to the Young's modulus of the top layer. Therefore, the fully organic system has a far smaller maximum interfacial shear stress compared with a metal/PDMS interface, which changes periodically during cyclic stretching. Because fatigue failure is quite sensitive to the amplitude of the stress, the smaller interfacial stress of the fully organic systems will be

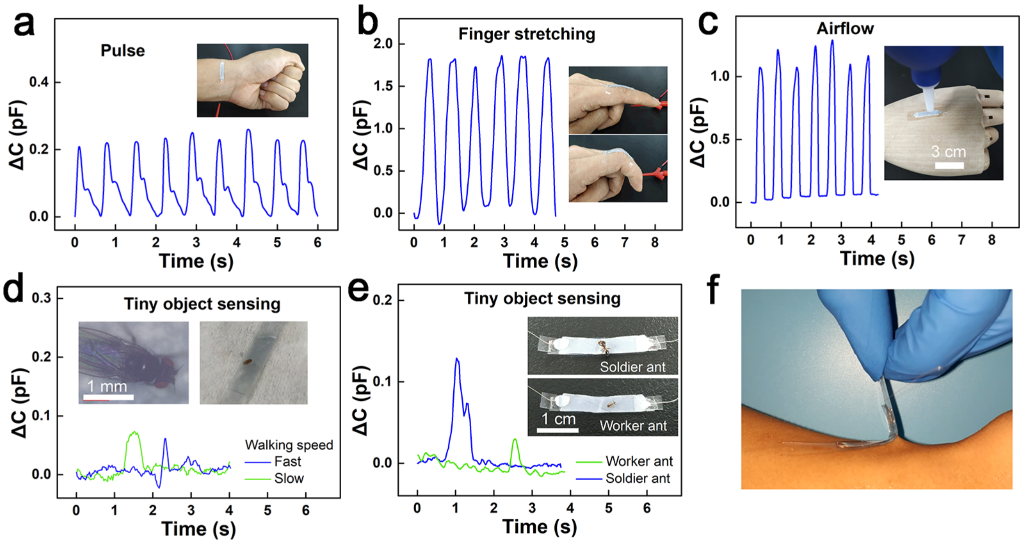

Figure 4. Applications of the fully organic iontronic skin. (a) Detection of blood pulse waveform of radical artery. (b) Signal caused by finger stretching. (c) Sensing of airflow caused by a suction bulb for a device mounted on a wooden artificial hand. (d) Detection of fruit flies at two different walking speeds. (e) Detection of ants with two different sizes. (f) Iontronic skin with sticky PDMS mounted on the skin.

quite helpful to achieve high interface reliability. Note that the strong interfacial strength also plays an important role for the high reliability. This sensitive, robust, and stretchable sensor is potentially useful in many circumstances, such as a wearable device for human health monitoring and moment detection or a sensitive skin for robots and artificial limbs. In Figure 4a,b, we show that our sensor can detect the blood pulse waveform with characteristic peaks of radical artery and body motion by finger bending which generates combined stretch and pressure input. Figure 4c demonstrates that the skin can give an artificial limb the ability to sense the external pressure caused by air flow. A special advantage of this skin is the ultralow LOD: Figure 4d,e shows that the device is capable of detecting tiny objects such as fruit flies and worker ants with mass less than 1 mg, which is corresponding to an ultralow pressure less than 0.1 Pa. The signals could well classify the ant type, a soldier, or a worker, as well as the walking speeds of the two tiny insects. Such weak mechanical signal can hardly be perceived by human hand or any reported e-skins. A human palm has high-density tactile sensors and is the most sensitive part of the human skin, however, we have verified that when a volunteer closed his eye, he was not able to judge whether there was a fruit fly walking or landing on his palm.

In addition, the device can also be directly mounted on the skin for epidermal electronics by tuning PDMS to be sticky (Figure 4f). PDMS is a material for which the elastic modulus, stretchability, and surface stickiness are well tunable, and this feature allows PDMS to be an ideal platform for stretchable electronics on the skin.[5,32] The high sensitive and soft e-skin may also be potentially used for other applications for which a stretchable, sensitive strain, and pressure sensor is required.

CONCLUSIONS

In this work, we combine the interfacial design and biaxial prestrain method to achieve a highly conductive, highly stretchable, and highly stable electrode and use the electrode for fully organic and intrinsically stretchable skin-like electronics. The PEDOT:PSS electrode shows little change of resistance at an extreme tensile strain of 100% and is free of fatigue over 10 000 cycles of stretching/releasing to 100% strain. A fully organic and intrinsically stretchable capacitive-type e-skin with the electrodes exhibits sensitive response to both normal compression with a maximum sensitivity of 7.00 kPa^{-1} and in-plane stretching with a maximum GF of 0.74, and is capable of detecting tiny objects beyond the detection limit of the human skin. The device also exhibits high stability under cyclic compression or cyclic stretches to 30%, and can be mounted on the skin by introducing sticky PDMS. The high robustness and stretchability of the fully organic e-skin lies in the wrinkle structures and small mechanical mismatch among different layers. Our method is a general strategy to make fully organic and intrinsically stretchable devices or systems that can be used in wearable electronics, epidermal electronics, and human−machine interfaces.

EXPERIMENTAL SECTION

Materials. PEDOT:PSS (Clevios PH 1000) was obtained from commercial sources. The cured PDMS film (BD KRN-200, thickness 200 μm) was purchased from Hangzhou Bald Advanced Materials. Co., Ltd. Benzophenone (BP) and methacrylic acid (MAAc) were purchased from Tokyo Chemical Industry Co., Ltd. Other reagents used were all in reagent grade. All materials were used as received.

Surface Modification of PDMS. The PDMS film was immersed in a 10 wt % BP/ethanol solution for 5 min and rinsed with methanol three times and dried in a vacuum oven for 10 min. After that, MAAc aqueous solution (20 wt %) was dropped on the PDMS surface, and a glass slide was then carefully covered on the droplet, creating a uniform and thin liquid layer. The thickness of the layer was controlled to be 0.1 mm by the aid of two spacers. Then, this set-up was placed under a UV-LED (wavelength 365 nm) radiation for 120 s. The obtained PDMS was further rinsed by ethanol and water.

Preparation of the PEDOT:PSS/g-PDMS Electrode. The PEDOT:PSS/glass electrode was first prepared by spin-coating PH 1000 solution (which is filtered through a 0.45 μm membrane) on the glass at 1000 rpm for 1 min, the films were then baked on a hot-plate at 130 °C for 10 min and post-treated by sulfuric acid. In this step, we droped certain amount of sulfuric acid solution (16 wt %) on the surface of the PEDOT:PSS/glass electrode at a hot-plate at 140 °C for 10 min and followed by washing with water and at last dried at 130 °C for another 10 min. Then, the g-PDMS was biaxially stretched to 100% in both direction using a homemade device, and the PEDOT:PSS/glass was placed on the substrate, 5 min later, the glass

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was peeled off and the electrode was obtained by releasing the strain. The process is shown in Figure S3.

Preparation and Test of Electronic Skins. The device consists of two pieces of PEDOT:PSS/g-PDMS electrodes sandwiching an ionic gel with surface microstructures. The ionic gel is composed of poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]). The detail of this microstructured ionic layer and the tests of the sensor can be found in our previous paper,[33] and all capacitance measurements in this work were conducted at a test frequency of 100 kHz.

Characterization. The sheet resistance of the electrode was measured using a four-probe tester. A homemade device was used for the mechanical−electrical property test at a strain rate of 50% s^{-1}, and detailed procedures are referred to our previous work.[34] The surface morphology of the films was characterized by OM, atomic force microscopy (AFM Bruker Dimension Edge), and SEM (TESCAN MIRA3). For the adhesion test, we used a 3M scotch tape to test the adhesion of PEDOT:PSS to p-PDMS and g-PDMS. The test was conducted within 30 min after the plasma treatment of PDMS.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b20255.

> Preparation and properties of g-PDMS, AFM image of PEDOT:PSS, performance of the electrode based on nongrafted PDMS, and performance of the electrode based on the uniaxial prestrain method (PDF)

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Notes

The authors declare no competing financial interest.

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